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Formation of methane hydrate from polydisperse ice powders

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Abstract

Neutron diffraction runs and gas-consumption experiments based on pressure-volum--temperature measurements are conducted to study the kinetics of methane hydrate formation from hydrogenated and deuterated ice powder samples in the temperature range of 245-270 K up to high degrees of transformation. An improved theory of the hydrate growth in a polydisperse ensemble of randomly packed ice spheres is developed to provide a quantitative interpretation of the data in terms of kinetic model parameters. This paper continues the research line of our earlier study which was limited to the monodisperse case and shorter reaction times (Staykova et al., 2003).1 As before, we distinguish the process of initial hydrate film spreading over the ice particle surface (stage I) and the subsequent hydrate shell growth (stage II) which includes two steps, i.e., an interfacial clathration reaction and the gas and water transport (diffusion) through the hydrate layer surrounding the shrinking ice cores. Although kinetics of hydrate formation at stage II is clearly dominated by the diffusion mechanism which becomes the limiting step at temperatures above 263 K, both steps are shown to be essential at lower temperatures. The permeation coefficient D is estimated as (1.46 ± 0.44) × 10-12 m2/h at 263 K with an activation energy QD ≈ 52.1 kJ/mol. This value is close to the energy of breaking hydrogen bonds in ice Ih and suggests that this process is the rate-limiting step in hydrate formation from ice in the slower diffusion-controlled part of the reaction. © 2006 American Chemical Society.

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